Improved Wide Operating Temperature Range of Li-Ion Cells

Applications include electric vehicles, where high-energy-density and high-power batteries are needed that can operate at low temperature.

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Future NASA missions aimed at exploring the Moon, Mars, and the outer planets require rechargeable batteries that can operate over a wide temperature range (–60 to +60 °C) to satisfy the requirements of various applications including landers, rovers, penetrators, CEV, CLV, etc. This work addresses the need for robust rechargeable batteries that can operate well over a wide temperature range.

The Department of Energy (DoE) has identified a number of technical barriers associated with the development of Li-ion rechargeable batteries for PHEVs. For this reason, DoE has interest in the development of advanced electrolytes that will improve performance over a wide range of temperatures, and lead to long life characteristics (5,000 cycles over a 10-year life span). There is also interest in improving the high-voltage stability of these candidate electrolyte systems to enable the operation of up to 5 V with high specific energy cathode materials.

Currently, the state-of-the-art lithium-ion system has been demonstrated to operate over a wide range of temperatures (–40 to +40 °C); however, the rate capability at the lower temperatures is very poor. In addition, the low-temperature performance typically deteriorates rapidly upon being exposed to high temperatures.

A number of electrolyte formulations were developed that incorporate the use of electrolyte additives to improve the high-temperature resilience, low-temperature power capability, and life characteristics of methyl propionate (MP)-based electrolyte solutions. These electrolyte additives include mono-fluoroethylene carbonate (FEC), lithium oxalate, vinylene carbonate (VC), and lithium bis(oxalate borate) (LiBOB), which have previously been shown to result in improved high-temperature resilience of all carbonate-based electrolytes. These MP-based electrolytes with additives have been shown to have improved performance in experiments with MCMB-$LiNiCoAlO_2$ cells.

A number of lithium-ion electrolytes having improved temperature range of operation were demonstrated. $LiPF_6$-based mixed carbonate electrolyte formulations that contain ester co-solvents have been optimized for operation at low temperature, while still providing reasonable performance at high temperature. In earlier work [see "Optimized Carbonate and Ester-Based Li-Ion Electrolytes" (NPO-44974) *NASA Tech Briefs*, Vol. 32, No. 4 (April 2008), p. 56], ester co-solvents, including methyl propionate (MP), ethyl propionate (EP), methyl butyrate (MB), ethyl butyrate (EB), propyl butyrate (PB), and butyl butyrate (BB), were investigated in multi-component electrolytes of the following composition: 1.0 M $LiPF_6$ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + X (20:60:20 v/v %) [where X = ester co-solvent]. Focusing upon improved rate capability at low temperatures (i.e., –20 to –40 °C), this approach was optimized further [see "Li-Ion Cells Employing Electrolytes With Methyl Propionate and Ethyl Butyrate Co-Solvents" (NPO-46976), *NASA Tech Briefs*, Vol. 35, No. 10 (October 2011), p. 47], which resulted in the development of 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 v/v %) and 1.20M $LiPF_6$ in EC+EMC+EB (20:20:60 v/v %), which were demonstrated to operate well over a wide temperature range in MCMB-$LiNiCoA1O_2$ and $Li_4Ti_5O_{12}$-$LiNiCoA1O_2$ prototype cells. In the current work, improved high temperature resilience, low temperature power capability, and life characteristics have been provided with methyl propionate-based electrolyte solutions [i.e., 1.20M $LiPF_6$ in EC+EMC+MP (20:20:60 v/v%)] possessing the additives described above.

This work was done by Marshall C. Smart and Ratnakumar V. Bugga of Caltech for NASA's Jet Propulsion Laboratory. Further information is contained in a TSP (see page 1).

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Non-Toxic, Non-Flammable, –80 °C Phase Change Materials

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The objective of this effort was to develop a non-toxic, non-flammable, –80 °C phase change material (PCM) to be used in NASA's ICEPAC capsules for biological sample preservation in flight to and from Earth orbit. A temperature of about –68 °C or lower is a critical temperature for maintaining stable cell, tissue, and cell fragment storage.

Within this technical effort, two phase change fluids were developed with melting onset at –85 °C and –61 °C, and latent heat of fusion of 100 and 136 J/mL, respectively. The experimental results

indicate good repeatability of the freeze/thaw cycle, compatibility with high-density polyethylene, thermal stability, and flashpoints exceeding 100 °C. Based on the individual components, the phase change fluids are expected to have low acute toxicity.

There are several types of phase change materials (PCMs) that can be considered for the preservation of biological samples at a temperature of about –68 ºC. These include hydrated salts in water, non-hydrated or weakly hydrated salts in water, non-electrolyte aqueous solutions, and pure, non-aqueous fluids. However, none of these options resulted in a –80 °C freezing point stable PCM during the freeze/thaw cycling. Therefore, a non-aqueous mixture was formulated yielding a pseudo melting point plateau, adequate stability over numerous thermal cycles, and suitable latent heats. The product is a non-aqueous base fluid with a somewhat tailored freezing point, and latent heats on the order of 100 J/mL for the –85 °C PCM.

The fluid developed is an organic solution with adequate resistance to biological growth, compatible with HDPE (high density polyethylene) plastic, and is characterized by a negative freezing expansion ratio. The negative expansion ratio during freezing will allow for the ICEPAC modules to be completely filled with PCM material as compared to previously used fluids requiring a 20-mL air bubble (within a 120-mL capsule). This translates to a 20-percent increase in cooling capacity for a given latent heat. Furthermore, the specific gravity of the PCM is on the order of 0.92 g/mL, making it lighter than an aqueous-based solution per ICEPAC capsule.

This work was done by J. Michael Cutbirth of Mainstream Engineering Corp. for Johnson Space Center. Further information is contained in a TSP (see page 1). *MSC-24460-1*

Soft-Bake Purification of SWCNTs Produced by Pulsed Laser Vaporization

A more efficient, cost-effective, environmentally friendly method purifies high-quality c arbon nanotubes.

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The "soft-bake" method is a simple and reliable initial purification step first proposed by researchers at Rice University for single-walled carbon nanotubes (SWCNT) produced by high-pressure carbon monoxide disproportionation (HiPco). Soft-baking consists of annealing as-produced (raw) SWCNT, at low temperatures in humid air, in order to degrade the heavy graphitic shells that surround metal particle impurities. Once these shells are cracked open by the expansion and slow oxidation of the metal particles, the metal impurities can be digested through treatment with hydrochloric acid.

The soft-baking of SWCNT produced by pulsed-laser vaporization (PLV) is not straightforward, because the larger average SWCNT diameters (≈1.4 nm) and heavier graphitic shells surrounding metal particles call for increased temperatures during soft-bake. A part of the technology development focused on optimizing the temperature so that effective cracking of the graphitic shells is balanced with maintaining a reasonable yield, which was a critical aspect of this study. Once the ideal temperature was determined, a number of samples of raw SWCNT were purified using the soft-bake method.

An important benefit to this process is the reduced time and effort required for soft-bake versus the standard purification route for SWCNT. The total time spent purifying samples by soft-bake is one week per batch, which equates to a factor of three reduction in the time required for purification as compared to the standard acid purification method. Reduction of the number of steps also appears to be an important factor in improving reproducibility of yield and purity of SWCNT, as small deviations are likely to get amplified over the course of a complicated multi-step purification process.

The full JSC characterization protocol consisting of UV-Vis-NIR absorption, Raman spectroscopy, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) was applied to all samples. In addition, the nanotube content as the percentage out of total carbon was calculated from UV-Vis-NIR absorption, using a procedure similar to that proposed in earlier research. The nanotube percentage relative to the total sample weight was calculated from the absorption data, taking into account the metal content. These measurements were used to quantify various aspects of the "quality" of the material in terms of: metal content (TGA residue weight percentage), oxidation temperature (the temperature of the most significant peak in the first derivative of the TGA), stability of DMF dispersion by optical absorption, nanotube content (weight percentage of total from UV-Vis-NIR absorption and TGA), the frequency of the Raman G-band peak, and the ratio between the D-band and G-band intensities. All measurements (except dispersion stability) were repeated three times to determine variability of the purification route through statistical methods. Standard deviations of the experimental results are considered important parameters to quantify the homogeneity of nanotube samples.

The data indicate that the major properties, such as metal content, nanotube content, oxidation temperature, and extent of defects as determined by Raman, are similar or superior for the soft-baked samples when compared to the standard acid-purified samples. TGA and Raman data suggest that there is more metal removed, less oxidative damage, less protonation, and less derivatization incurred from the acid treatment in soft-baked samples. The stability and reproducibility of DMF dispersions is also superior, suggesting that soft-baking leads to greater homogeneity in materials than standard acid purification routes.

The observed improvement in efficiency translates directly into greater yield and quality of nanotubes, reduced cost and processing time, and the use of lesser amounts of organic solvents and concentrated acids, making the process safer and more environmentally friendly. This approach, as